AD-A215 078

(2)

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

DTIC
ELECTE
NOV 29 1989
S D
D
Cs

1a. REPORT SECURITY CLASSIFICATION

1b. RESTRICTIVE MARKINGS

2a. SECURITY CLASSIFICATION AUTHORITY

2b. DECLASSIFICATION/DOWNGRADING SCHEDULE

3. DISTRIBUTION/AVAILABILITY OF REPORT

DISTRIBUTION STATEMENT A
Approved for public release;
Distribution Unlimited

4. PERFORMING ORGANIZATION REPORT NUMBER(S)
03

5. MONITORING ORGANIZATION REPORT NUMBER(S)

6a. NAME OF PERFORMING ORGANIZATION
Northwestern University

6b. OFFICE SYMBOL *(If applicable)*

7a. NAME OF MONITORING ORGANIZATION

6c. ADDRESS *(City, State and ZIP Code)*
Department of Chemistry
Evanston, Illinois 60208-3113

7b. ADDRESS *(City, State and ZIP Code)*

8a. NAME OF FUNDING/SPONSORING ORGANIZATION
Office of Naval Research

8b. OFFICE SYMBOL *(If applicable)*

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER

8c. ADDRESS *(City, State and ZIP Code)*
Department of the Navy
Arlington, Virginia 22217

10. SOURCE OF FUNDING NOS.

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT NO.

11. TITLE *(Include Security Classification)*
Linear Free Energy Relation for ...

12. PERSONAL AUTHOR(S)
M. S. Ram and Joseph T. Hupp

13a. TYPE OF REPORT
Technical Report

13b. TIME COVERED
FROM ________ TO ________

14. DATE OF REPORT *(Yr., Mo., Day)*
11/89

15. PAGE COUNT
15

16. SUPPLEMENTARY NOTATION

17. COSATI CODES

FIELD	GROUP	SUB. GR.

18. SUBJECT TERMS *(Continue on reverse if necessary and identify by block number)*

19. ABSTRACT *(Continue on reverse if necessary and identify by block number)*

A comparison is made between electrochemical and homogeneous redox reactivity for species involving the transfer of multiple electrons at a single thermodynamic potential. In the electrochemical case the co-reactant is the electrode; in the homogeneous case it is any of several members of a homologous series of one-electron reagents. In the latter case it is shown that the slope of a plot of the observed pseudo first order rate constant (one-electron reagent in excess) versus the thermodynamic driving force can be used to identify the cross reaction's rate-determining step. It is noted that the proposed use of a homogeneous linear free energy relation (Bronsted plot) for mechanistic purposes is closely analogous to the well known Tafel approach (log current vs. potential) in electrochemical kinetics.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT
UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS ☐

21. ABSTRACT SECURITY CLASSIFICATION

22a. NAME OF RESPONSIBLE INDIVIDUAL
Joseph T. Hupp

22b. TELEPHONE NUMBER *(Include Area Code)*
(708) 491-3504

22c. OFFICE SYMBOL

DD FORM 1473, 83 APR

EDITION OF 1 JAN 73 IS OBSOLETE.

SECURITY CLASSIFICATION OF THIS PAGE

OFFICE OF NAVAL RESEARCH

TECHNICAL REPORT

FOR

Contract N0014-88K-0369

Technical Report No. 3

Linear Free Energy Relations for Multielectron Transfer Kinetics: A Brief Look at the Bronsted/Tafel Analogy

by

M. S. Ram and Joseph T. Hupp*

(708) 491-3504

Department of Chemistry

Northwestern University

Evanston, Illinois 60208-3113

Accesion For
NTIS CRA&I ✓
DTIC TAB
per CB
A-1

Reproduction in whole, or in part, is permitted for any purpose of the United States Government.

** Accepted for publication in J. Phys. Chem.

Introduction

One of the recurring themes in kinetic studies of single electron transfer (ET) reactions at electrochemical interfaces is that much can be learned by simple analogy to related reactions in homogeneous solution.[1] Electrochemists, at least, also like to believe that the converse is true: insights regarding homogeneous electron transfer reactivity can be derived from electrochemical investigations. We are seeking to apply both principles in our emerging studies of multielectron transfer kinetics. In this communication we explore one particular aspect of multi-ET reactivity – the dependence on thermodynamic driving force. Starting from an electrochemical perspective, we develop a fairly simple homogeneous analog. We then collect the observations and reflect briefly on the possible broader significance of linear free energy relations for multi-ET processes.

In the area of electrochemical kinetics there exists a long and successful history of utilizing linear free energy relations to ascertain the mechanistic details of interfacial rate processes.[2] Experimentally these relations take the form of so-called "Tafel plots", i.e. plots of ln i (or sometimes ln k) versus the electrochemical potential, E. In the plots, i is the diffusion-corrected and back-reaction-corrected current – in other words the net electrochemical *rate*. Alternatively, k is the first-order heterogeneous *rate constant* (cm s^{-1}). In either case the slope of the plot is $\pm\alpha F/RT$ where α is the transfer coefficient and F is the Faraday constant. Perhaps the most significant point is that α behaves as an electrochemical "Bronsted coefficient";[2a] within the context of transition-state theory, therefore, α can be identified approximately as $n\partial\Delta G^{\star}/\partial\Delta G$. (Here $\Delta G^{\star}$ is the experimental activation free energy, while ΔG is the overall (n electron) thermodynamic driving force. The driving force is equivalently given by $\pm nF(E - E_f)$, where E_f is the formal reduction potential and the sign distinguishes oxidation from reduction.)

In electrochemical studies the Tafel approach is particularly helpful when a reaction requires the transfer of multiple electrons at a single thermodynamic potential, but in kinetically distinct one-electron steps. It is well known that under these conditions the value of α precisely prescribes the integral number of electrons transferred in any rapid equilibria preceding the rate-determining step. For example, if no electrons precede the slowest step (i.e. the first electron is rate determining), α will equal roughly 0.5.[3] If one electron transfer precedes the rate-determining ET step (i.e. the second electron is rate determining), α will equal approximately 1.5. If two electron transfers precede the rate determining step (i.e. the third electron is rate determining) α will equal 2.5 and so on. Furthermore, from the principle of microscopic reversibility the sum of α values in the forward and reverse directions at any given electrochemical potential should equal the total number of electrons transferred.

Tafel measurements clearly are powerful diagnostic tools in electrochemical kinetic studies. We were interested therefore, in ascertaining whether a complementary method might exist for homogeneous processes. We find that indeed one does. What follows is an informal derivation. For concreteness the derivation is presented in terms of a specific (hypothetical) homogeneous cross reaction. In general, however, the reactions of interest are those involving a multi-electron redox couple and a homologous series of one-electron co-reactants.

Derivation of Homogeneous Driving Force Relationships

Consider the three electron, three proton reduction of chelated Os(VI):[4]

$$Os^{VI}(terpyridine)(O)(OH)(OH_2)^{3+} + 3e^- + 3H^+ \longrightarrow Os^{III}(terpyridine)(OH_2)_3{}^{3+} \quad (1)$$

Although eq. 1 can be driven electrochemically, it should also be possible to effect the reduction homogeneously with a one electron reagent. If a series of closely related reagents is prepared (say, $Ru^{II}(NH_3)_5(pyridine\text{-}X)^{2+}$ where $X = H, CH_3, Br, NO_2$, etc.) the members of the series will likely display different redox potentials but similar self-exchange rates. From a series of rate measurements, one should be able to construct a "Bronsted" plot of log rate vs. driving force (by analogy to similar plots for Bronsted acid catalysis) and perhaps derive mechanistic information.

The reduction of Os(VI) by any particular member of the series presumably occurs sequentially as follows:

$$Os(VI) + Ru(II) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Os(V) + Ru(III) \quad (2)$$

Defining E_1 as the reduction potential of the Os(VI/V) couple, E_{Ru} as the potential for the Ru(III/II) couple and K_1 as the equilibrium constant for eq. 2, we find that

$$E_1 - E_{Ru} = (RT/F) \ln K_1 \quad (3)$$

and

$$K_1 = k_1/k_{-1} \quad (4)$$

where k_1 and k_{-1} are the second order rate constants for the forward and reverse reactions in eq. 1. Similarly, if we assume:

$$Os(V) + Ru(II) \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Os(IV) + Ru(III) \tag{5}$$

we obtain:

$$E_2 - E_{Ru} = (RT/F) \ln K_2 \tag{6}$$

and

$$K_2 = k_2/k_{-2} \tag{6}$$

where E_2 is the Os(V/IV) redox potential and K_2, k_2 and k_{-2} are the respective equilibrium and rate constants. Finally, we may write

$$Os(IV) + Ru(II) \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} Os(III) + Ru(III) \tag{8}$$

$$E_3 - E_{Ru} = (RT/F) \ln K_3 \tag{9}$$

and

$$K_3 = k_3/k_{-3} \tag{10}$$

where E_3 is the Os(IV/III) redox potential and K_3, k_3 and k_{-3} are the respective equilibrium and rate constants. The net process thus is

$$Os(VI) + 3Ru(II) \rightleftharpoons Os(III) + 3Ru(III) \tag{11}$$

By applying a steady-state approximation to the unstable intermediates (Os(V) and Os(IV)) we can obtain several rate expressions. When eq. 2 is rate determining

$$d[Os(III)]/dt = (1/3)d[Ru(III)]/dt = k_1[Os(VI)][Ru(II)] \tag{12}$$

When eq. 5 is rate determining

$$d[Os(III)]/dt = (1/3)d[Ru(III)]/dt = \frac{k_1\ k_2[Os(VI)][Ru(II)]^2}{k_{-1}[Ru(III)] + k_2[Ru(II)]} \qquad (13)$$

When eq. 8 is rate determining

$$d[Os(III)]/dt = (1/3)d[Ru(III)]/dt = \frac{k_1\ k_2\ k_3[Os(VI)][Ru(II)]^3}{k_{\ 1}[Ru(III)] + k_{-1}\ k_{-2}[Ru(III)]^2 + k_3[Ru(II)]^2} \qquad (14)$$

If Ru(II) were used in great excess over Os(VI) and if all steps preceding the rate determining step were in rapid equilibrium, then the following expressions for the observed pseudo-first order rate constant would apply. When eq. 2 is rate determining:

$$k_{obs} = k_1[Ru(II)] \qquad (15)$$

When eq. 5 is rate determining:

$$k_{obs} = K_1\ k_2[Ru(II)]^2/[Ru(III)] \qquad (16)$$

When eq. 8 is rate determining:

$$k_{obs} = K_1\ K_2\ k_3[Ru(II)]^3/[Ru(III)]^2 \qquad (17)$$

where $k_{obs} = -(1/[Os(VI)])(d[Os(VI)]/dt)$ and $-d[Os(VI)]/dt = d[Os(III)]/dt$ in eqs. 15-17.[5]

Experimentally, any fractional order with respect to Ru(II) would suggest that the equilibria prior to the rate-determining step are not rapid and that some steps occur concurrently. (It is also worth considering the reverse experimental condition. If Os(VI) were used in pseudo first order excess instead of Ru(II), and if eq. 2 were rate determining, k_{obs} would equal

$3k_1[\mathrm{Os(VI)}]$. On the other hand, if either eq. 5 or 8 were slow, non-pseudo-first-order kinetics with respect to [Ru(II)] would be expected, despite the large excess of Os(VI) (cf. eqs. 12-14).)

In general, when m one-electron steps precede the rate determining step

$$k_{obs} = K_1 K_2 \ldots K_m k_{rds}[R]^{m+1}/[O]^m \qquad (18)$$

where R and O represent the reduced and oxidized forms of the one-electron reductant. In fact, under the assumption that all steps prior to the rate determining step are occurring as rapid preequilibrium processes, and with excess added O (such that its concentration is essentially constant), the order with respect to R will indicate which step in the multi-electron transfer is rate determining.

If we assume that a linear free energy relationship (eq. 19) can be applied to the rate determining step (analogous, in a sense, to a Bronsted acid catalysis expression) then eq. 20 can be obtained by combining eqs. 18 and 19:

$$\ln k_{rds} = \beta \ln(K_{m+1}) + \gamma \qquad (19)$$

$$\ln k_{obs} = (E_1 - E_R)F/RT + (E_2 - E_R)F/RT + \ldots + (E_m - E_R)F/RT + \beta(E_{m+1} - E_R)F/RT + (m + 1)\ln[R] - m \ln[O] + \ln k^\circ_{rds} \qquad (20)$$

(In eq. 20, k°_{rds} is the value of k_{rds} when the overall free energy driving force is zero. Also, it is assumed that the dimensions of the last three terms are chosen so as to render the composite logarithmic term unitless.) Thus, if we have a series of one-electron reductants whose potentials (E_R) vary, a plot of $\ln k_{obs}$ vs. E_R should be linear with a slope of $m + \beta$ (for a fixed concentration of the reductant and with enough added oxidized form such that

[O] is effectively constant during the course of the reaction). This type of experiment is a precise homogeneous analog of the electrochemical Tafel experiment (ln i vs. E) and for a multi-electron transfer reaction yields the same information (m and α values). If Marcus-type behavior were obeyed for the rate determining step in the homogeneous reaction, the value of β would generally be close to 0.5.[3] Thus from the slope of the Bronsted plot the value of m would be obtained, where m + 1 would designate the slow step in the overall kinetic process.

When the reverse of eq. 11 can be studied with the same reagents and a second Bronsted plot constructed, the slope can be shown (by microscopic reversibility) to equal $n - m - 1 + \beta'$ where $\beta' = 1 - \beta$ and m is determined from the forward kinetics (see above). It also follows that the two Bronsted plots will intersect at the overall formal potential for the multi-electron couple[6] (provided that any stoichiometric factors implicit in the plots have been handled in a consistent way).

Potential Limitations

It should be noted that in the derivation several assumptions have been made, including the following: 1) All steps prior to the rate determining step occur as rapid pre-equilibria. 2) With a series of one-electron transfer reagents, only the potential of the reagent varies, but not its intrinsic reactivity (i.e. self-exchange rate). 3) The rate determining step in the multi-ET cross reaction remains constant throughout the series. 4) A steady state approximation is acceptable for the concentrations of species in unstable intermediate oxidation states. 5) Whenever the first step is not rate determining, both the oxidized and reduced forms of the one-electron reagent are present in sufficient amounts that their concentrations remain effectively constant throughout the reaction. 6) Extraneous parameters such as pH, ionic strength and temperature remain fixed for a given reaction series. Obviously in any particular experiment one or more of the assumptions might be invalid and suitable corrections would need to be applied. Nevertheless the framework of assumptions is not really very much more restrictive than in electrochemical Tafel studies.

Following on from the above, we find in particular that two of the more obvious chemical complications - disproportionation of redox intermediates (e.g. Os (V) or Os (IV) in the example above)[7] and "square scheme" coupling of electron transfer to proton transfer[8] - do not *necessarily* vitiate the multielectron Bronsted analysis. However, a third possible complication - the occurrence of inner-sphere pathways - is more problematic. Just as with the Marcus one-electron cross relationship,[9,10] there is no reason to believe *a priori* that the multielectron driving-force analysis will be applicable when reactions proceed by ligand-bridged pathways. In fact, in many such instances it may not even be useful to view the reaction in terms of sequential one-electron steps. Such limitations obviously will circumscribe to a large extent the applicability of the analysis to true catalytic reactions. On the other hand, the same is true of the Marcus cross relationship. The Bronsted analysis still might prove useful, however, as a benchmark against which catalytic multielectron redox reactivity could be evaluated.

Possible Applications

Ideally on would like to illustrate the above analysis with kinetic data for a "real" system. Unfortunately we have been unable to identify a suitable reaction series. [A significant number of examples do exist for the sequential one-electron reduction (or oxidation) of multielectron redox species (most notably, chromate) by isolated single-electron reagents.[5b] Unfortunately, in almost no instance (to our knowledge) has the identity of the single-electron reagent been varied in a systematic fashion.[11,12] This should perhaps not be too surprising since, in the absence of the present analysis, there would be no compelling reason to pursue such an investigation.] Also, preliminary studies in our laboratory[13] of a three-electron osmium/ruthenium series (comparable to the one described above) were thwarted by an inability to monitor adequately (by stopped-flow methods) the relatively rapid ET kinetics. Nevertheless, given the recent proliferation of both synthetic and mechanistic activity involving related transition-metal oxo/aquo species[14] it seems reasonable to suppose that many examples of Bronsted-type multielectron reactivity will eventually become available.

Despite the shortage of existing illustrative examples, it may be worth speculating briefly on what other kinds of redox studies might possibly be facilitated by the proposed analysis. Two examples come to mind, based on our own current research interests. The first involves the electrochemical oxidation and reduction of solution species by hydrous oxide surfaces.[15] These surfaces can display both univalent (e.g. Ir(III/IV)) and divalent (e.g. Ir(IV/VI) or Ru(IV/VI)) redox phase transformations. Whether these transformations correspond to the discrete (i.e. localized) oxidation and reduction of an array of metal sites or alternatively, to electrochemical band depletion and filling is, at present, a point of controversy. (Indeed, some evidence suggests that both types of electronic behavior may exist — the determining chemical factor being the extent of metal-oxide hydration.[15])

Regardless of the details, if the oxide surface were to function as a redox mediator[16] (i.e., if electron transfer to and from solution species were to entail repetitive cycling between different oxide valence states) the reaction kinetics would be formally analogous to those for homogeneous processes. In attempting to unravel the kinetics, however, there could be substantial difficulties in usefully varying the metal-oxide concentration and thereby determining an oxide reaction order. On the other hand, a Bronsted-type analysis of oxide reactivity (based on a homologous series of solution species) might provide an alternative route to the desired information. The second example is closely related. It would involve hybrid reactions between solution redox species and species immobilized in a polymeric film, at an electrode surface.[17] Depending on just how the immobilization were carried out, there might again be difficulties in achieving systematic variations in concentration for the incorporated species and therefore, in ascertaining a reaction order in the conventional fashion. The proposed driving-force analysis, however, might well provide a viable route to the same information.

Concluding Comments: An Implication for Heterogeneous Systems

As indicated above, a homogeneous analog of the electrochemical Tafel analysis can be formulated for multi-electron reagents. The simple derivation offered here[18] highlights the relation between Bronsted slopes and reaction orders. From the derivation one might reasonably conclude that a suitable alternative interpretation for the transfer coefficient in the corresponding heterogeneous (electrochemical) experiment would be in terms of an effective reaction order in the electron.[19] Although the usual preference in electrochemical kinetics is to express reactivity exclusively in terms of potentials and currents (i.e. without specific regard for the electron itself as a reactant) the reaction-order analogy offered by the multielectron Bronsted analysis is (at least in a formal sense) very appealing. We hope to explore the concept further in ongoing experimental studies.

Acknowledgement.

This work was supported by a grant from the Office of Naval Research.

References

1. See, for example: Weaver, M. J. in Comprehensive Chemical Kinetics, vol. 27, R. G. Compton, Ed., Elsevier, Amsterdam, 1988.
2. (a) Albery, W. J., "Electrode Kinetics", Oxford University Press, Oxford, 1975. (b) Vetter, K. J., "Electrochemical Kinetics", Academic Press, New York, 1967. (c) Bockris, J. O'M.; Reddy, A. K. N., "Modern Electrochemistry", Vol. 2, Ch. 9, 10, Plenum Press, New York, 1970
3. In principle, α (or β) for a one-electron transfer can differ substantially from 0.5 when the reaction is extremely exothermic ($\alpha \rightarrow 0$), extremely endothermic ($\alpha \rightarrow 1$), when large work terms exist, or when force constants for internal-coordinate displacements are strongly oxidation-state dependent.
4. Pipes, D. W.; Meyer, T. J., Inorg. Chem., 1986, 25, 4042.
5. We note that up to this point the derivation is fairly routine and that rate laws analogous to eqs. 12, 13, 15 and 16 can be found, in particular, in the extensive literature on Cr(VI) redox chemistry. See, for example: (a) Espenson, J. H., Acc. Chem. Res., 1970, 3, 347. (b) Beattie, J. K.; Haight, J. P., Prog. Inorg. Chem., 1972, 17, 93.
6. This is just a statement, of course, that the forward rate constant must equal the reverse when $\prod_{i=1}^{m+1} K_i$ is unity.
7. Obviously, however, very rapid disproportionation would modify and complicate the overall scheme for multielectron transfer. Nonetheless, the proposed Bronsted analysis should still prove successful, in many instances, in identifying the slow single-electron-transfer step preceding disproportionation.

8. For a succinct description of square scheme kinetics in the context of *electrochemical* reactions see ref. 2a, chapter 5.

9. Marcus, R. A., J. Chem. Phys., 1965, 45, 679.

10. Newton, T. W., J. Chem. Ed., 1968, 45, 571.

11. An exception apparently is the sequential conversion of oxygen to hydrogen peroxide by a series of bis(phenanthroline)copper(I) complexes (Goldstein, S.; Czapski, G., Inorg. Chem., 1985, 24, 1087). Here, however, the second one-electron reduction ($CuL_2^+ + O_2^- + 2H^+ \longrightarrow CuL_2^{2+} + H_2O_2$) fails to display Marcus-type behavior, thereby ruling out "simple" electron transfer (or proton coupled electron transfer) as the redox mechanism.

12. A system which comes close to fulfilling the criteria we would find ideal for application of the Bronsted analysis is the two-electron oxidation of a series of phenols by Fe(phenanthroline)$_3^{3+}$ (Kimura, M.; Kaneko, Y., J. Chem. Soc. Dalton Trans., 1984, 341). Unfortunately, in this system it is the potential of the multielectron reagent (rather than FeL_3^{3+}) that is systematically varied. Furthermore, the available evidence indicates that the oxidation proceeds by a relatively uninteresting mechanism (from our perspective) that is illustrated here (albeit, in the reverse direction) by eq. 2 (i.e. in the two-electron phenol oxidation the first electron transfer is rate determining).

13. Ram, M. S., unpublished.

14. For an excellent (but already somewhat dated) review, see: Meyer, T. J., J. Electrochem. Soc., 1984, 131, 221C.

15. Burke, L. D. in "Modern Aspects of Electrochemistry", White, R. E.; Bockris, J. O'M.; Conway, B. E., Editors, Vol. 18, Plenum Press, New York, 1986.

16. Burke, L. D.; Healy, J. F.; O'Dwyer, K. J.; O'Leary, W. A., *J. Electrochem. Soc.*, 1989, *136*, 1015.

17. For a representative report involving a single electron transfer, see: Leidner, C. R.; Murray, R. W., *J. Am. Chem. Soc.*, 1984, *106*, 1606.

18. Related derivations for electrochemical reactions can be found in refs. 2b (pp. 149-154) and 2c (ch. 9).

19. Concepts akin to an "electrode reaction order" have occasionally appeared in the electrochemical literature (see, for example: Anson, F. C., *J. Electroanal. Chem.*, 1973, *47*, 279). Invariably, however, these have referred to a kinetic stoichiometry in surface coordination or adsorption sites, or to some closely related idea. The suggestion here is distinctly different: the relevant entity is the electron itself (or hole, if the reaction were an oxidation). It should be noted that the more conventional approach to reaction order assessment (i.e. variation of the reagent concentration and subsequent rate evaluation) would almost certainly be unsuccessful in the case of an electron from an electrode. The problem, of course, is that the supply of electrons having the ability to cross the electrode/solution interface (i.e. the current) cannot be controlled independently of the electrode potential (i.e. the free energy of the transferring electron). (On the other hand, a conventional concentration-based reaction-order analysis probably could be envisioned if electrons were to be delivered instead by a technique such as pulsed radiolysis. The cost, however, would be the complete loss of ability to modulate the electron's free energy - a key element in electrode kinetics In other words, the externally variable supply of electrons would be deliverable only at a single, fixed and predefined energy.)